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J. MACROMOL. SCI.—REVS. MACROMOL. CHEM., C3(1), 69-103 (1969) n 1. 1

Cross-Linking—Effect on Physical Properties of Polymers

LAWRENCE E. NIELSEN

Monsanto Company and Washington University
St. Louis, Missouri

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I. INTRODUCTION

Many of the polymers used in composite systems and in other applications are cross-linked or thermoset polymers. How do such cross-linked polymers differ in properties from the better-understood linear or thermoplastic polymers? This review paper attempts to answer this question. The paper is written from the practical viewpoint of the experimental scientist who is using cross-linked polymers but who is not an expert on the theory of cross-linking.

In spite of their intractable nature once they have been formed, and the difficulty of fabricating highly cross-linked polymers, such materials have some outstanding properties that make them ideal for many applications. The properties include (1) excellent dimensional stability and low creep rates, (2) resistance to solvents, and (3) in many cases, high heat-distortion or softening temperatures.

Cross-linked structures can be made in essentially two ways: (1) the tying together of long linear polymer molecules to give an infinite network structure; (2) the building up of low-molecular-weight multifunctional molecules to give higher-molecular-weight branched structures and, eventually, continuous cross-linked structures. An example of the first type is the vulcanization of rubber, while condensation polymerizations containing some tri- or tetra-functional molecules are examples of the second type.

In addition to vulcanized rubbers, typical cross-linked polymers include phenol-formaldehyde resins, melamine resins, cross-linked polyester resins, and epoxy resins.

CROSS-LINKING-EFFECT ON PHYSICAL

The theory of gelation and cross-linking in the classical work of Flory [1] shows that a critical structure or gelation does not occur until a critical action has progressed to a critical

$$b_c = \frac{1}{f-1}$$

b_c is the critical value of the branching coefficient defined as the probability that a given linking agent will lead along a chain to another linking agent. f is the functionality of the cross-linking agent. The branching coefficient b is related to the extent of reaction. For instance, in the formation of a cross-linked polymer by reacting a difunctional alcohol with a trifunctional alcohol in stoichiometric proportions, the branching coefficient is related to the extent of

$$b = \frac{p^2 \theta}{1 - p^2(1 - \theta)}$$

where θ is the ratio of hydroxyl groups belonging to the trifunctional alcohol to the total hydroxyl groups in the mixture. Thus, if the extent of reaction is $p = (\frac{1}{2})^{1/2} \approx 0.707$, the reaction is nearly complete at this extent of reaction. In many molecules not attached to the cross-linking of long-chain polymers by case of vulcanization of rubber, the cross-linkage for each two of the hydroxyl groups is a very small amount of cross-linking. In actual systems, the simple and the basic assumptions of the theory and the resulting mathematical equations are over-simplified.

II. WAYS OF CHARACTERIZING

Since cross-linked networks are not soluble, it is important to have technical parameters—such as the cross-link density or the weight of chains between cross-links—

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INTRODUCTION

In composite systems and in other or thermoset polymers. How do such in properties from the better-under-polymers? This review paper attempts paper is written from the practical scientist who is using cross-linked pert on the theory of cross-linking. le nature once they have been formed, y highly cross-linked polymers, such ing properties that make them ideal operties include (1) excellent dimen-rates, (2) resistance to solvents, and istoriton or softening temperatures. n be made in essentially two ways: near polymer molecules to give an the building up of low-molecular-es to give higher-molecular-weight tually, continuous cross-linked struc-type is the vulcanization of rubber, tions containing some tri- or tetra-ples of the second type. bbers, typical cross-linked polymers esins, melamine resins, cross-linked stns.

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The theory of gelation and cross-linking is described in detail in the classical work of Flory [1] and others [2,3]. Infinite network structure or gelation does not occur until the polymerization reaction has progressed to a critical value which is determined by

$$b_c = \frac{1}{f-1} \quad (1)$$

b_c is the critical value of the branching coefficient b , which is defined as the probability that a given functional group of a cross-linking agent will lead along a chain to another cross-linking unit. f is the functionality of the cross-linking agent. If $f = 3$, then $b_c = \frac{1}{2}$. The branching coefficient b is related to the extent of the polymerization reaction. For instance, in the special case of polyesters formed by reacting a difunctional acid with a mixture of di- and tri-functional alcohols in stoichiometric amounts, the branching coefficient is related to the extent of reaction p by

$$b = \frac{p^2 \theta}{1 - p^2(1 - \theta)} \quad (2)$$

where θ is the ratio of hydroxyl groups (reacted and unreacted) belonging to the trifunctional alcohol to the total number of hydroxyl groups in the mixture. Thus, if the mixture contains just the acid and trifunctional alcohol ($\theta = 1$), gelation should occur when the extent of reaction is $p = (\frac{1}{2})^{1/2} = 0.707$. Of course, gelation is not nearly complete at this extent of reaction, and the gel contains many molecules not attached to the network structure. In the cross-linking of long-chain polymers by a cross-linking agent, as in the case of vulcanization of rubber, gelation starts when there is one cross-linkage for each two of the original polymer molecules. Thus a very small amount of cross-linking agent can bring about gelation. In actual systems, the simplicity of the theoretical models and the basic assumptions of the theories may not be realized, so the resulting mathematical equations are, at best, only approximate and over-simplified.

II. WAYS OF CHARACTERIZING CROSS-LINKED NETWORKS

Since cross-linked networks can have a great variety of structures, it is important to have techniques to characterize these structural parameters—such as the cross-link density or the molecular weight of chains between cross-links, the distribution in the length

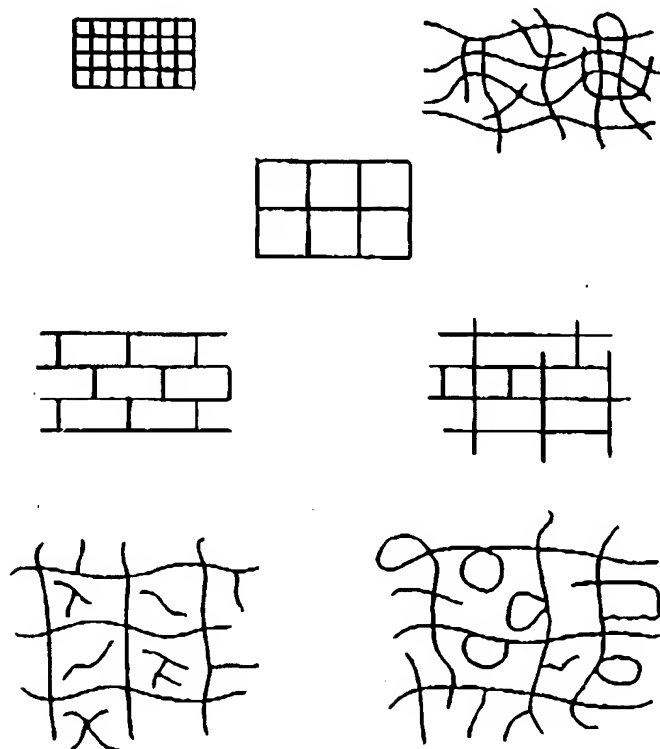


Fig. 1. Schematic diagram of some different types of cross-linked networks.

of chains between cross-links, the perfection of the network, and the amount of polymeric material not attached to the network. Figure 1 symbolically illustrates a few of the possible types of network structures that might be expected. Networks can be regular, highly irregular, tightly cross-linked, loosely cross-linked, highly imperfect with intramolecular loops and many free ends and molecules trapped in the network but unattached to it, or combinations of the above. The cross-link junctures can be trifunctional or tetrafunctional. Thus,

CROSS-LINKING—EFFECT ON PHYSICAL P

compared to the characterization of the weights of a linear polymer, the characterization of a cross-linked polymer is much more difficult. To make matters even worse, the available methods for determining the molecular weights of cross-linked polymers are as those used to determine the molecular weights of linear polymers. Therefore, the best that can be done for cross-linked systems is to get some kind of estimate of the number of cross-links and a measure of the perfection of the network.

Methods of studying network structure

1. chemical methods.
2. swelling solvents.
3. elastic moduli above the glass-transition temperature.
4. creep (for rubbers).
5. mechanical damping (for rubbers).
6. shift in glass-transition temperature.

If one knows the concentration of a cross-linking agent that reacts completely according to one's knowledge of the chemical reaction, it is possible to determine the molecular weight \bar{M}_c of polymer between cross-links. These chemical methods give only approximate results.

In the past, most of the effort has been directed toward the work structure of rubbers or polymers above their glass-transition temperature T_g . Less effort has been directed toward characterizing highly cross-linked polymers below T_g , such as vulcanized rubbers or where the available methods are invalid. Practically nothing has been done in the rigid state below their T_g , where the nature of any cross-linking is different.

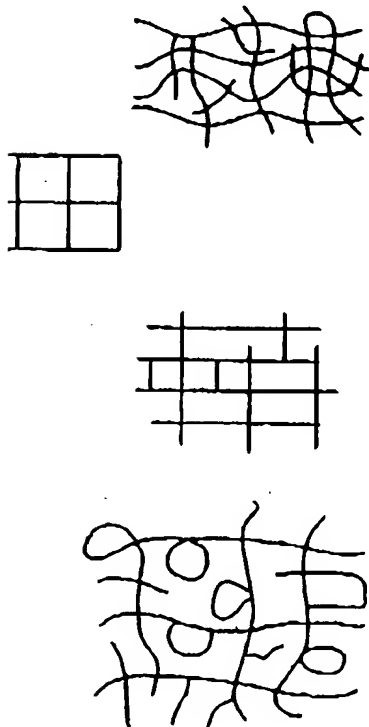
If an uncross-linked polymer is swollen, a cross-linked polymer will swell less. The swelling behavior of lightly cross-linked polymers is fairly complete [1]. Three types of measurements are used: (1) the amount of swelling; (2) the amount of swelling into the network structure and, therefore, the gel fraction; (3) the molecular weight of swelling of the gel fraction. Swelling is defined as follows:

$$\text{Swelling ratio } q = \frac{\text{Volume of swollen polymer}}{\text{Volume of dry polymer}}$$

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c different types of cross-linked networks.

the perfection of the network, and the not attached to the network. Figure 1 of the possible types of network structure. Networks can be regular, highly irregularly cross-linked, highly imperfect many free ends and molecules trapped to it, or combinations of the above. trifunctional or tetrafunctional. Thus,

compared to the characterization of the distribution in molecular weights of a linear polymer, the characterization of the structure of a cross-linked polymer is much more complex and difficult. To make matters even worse, the available techniques are not as good as those used to determine the molecular weights of linear, soluble polymers. Therefore, the best that can be done with most cross-linked systems is to get some kind of an average density of cross-links and a measure of the perfection of the network.

Methods of studying network structures include:

1. chemical methods.
2. swelling solvents.
3. elastic moduli above the glass-transition temperature.
4. creep (for rubbers).
5. mechanical damping (for rubbers).
6. shift in glass-transition temperature.

If one knows the concentration of a cross-linking agent, and if it reacts completely according to one's hypotheses about the nature of the chemical reaction, it is possible to estimate the average molecular weight \bar{M}_c of polymer between cross-links. Generally, however, these chemical methods give only approximate estimates.

In the past, most of the effort has been to characterize the network structure of rubbers or polymers above their glass-transition temperature T_g . Less effort has been concentrated on characterizing highly cross-linked polymers beyond the practical range of vulcanized rubbers or where the available theories tend to become invalid. Practically nothing has been done to characterize materials in the rigid state below their T_g , where most properties are insensitive to the nature of any cross-linked network that might be present.

If an uncross-linked polymer is soluble in a liquid, then the same polymer when cross-linked will swell in the liquid. The theory of the swelling behavior of lightly cross-linked polymers in liquids is fairly complete [1]. Three types of data can be obtained from swelling measurements: (1) the amount of polymer that is not incorporated into the network structure and, therefore, can be extracted as a sol fraction; (2) the molecular weight of the sol fraction; (3) the amount of swelling of the gel fraction. Swelling is generally expressed as a swelling ratio q defined as follows:

$$\text{Swelling ratio} = q = \frac{\text{Volume of swollen gel}}{\text{Volume of unswollen gel}}$$

The soluble part of the material or sol fraction is defined as

$$\text{Sol fraction} = \frac{\text{Weight of soluble material extractable}}{\text{Initial weight of material}}$$

The three quantities characterizing a cross-linked polymer are theoretically not independent. However, in most practical situations we do not know enough about the cross-linking reactions and their kinetics to apply theory properly, so all three quantities should be measured.

The swelling of a cross-linked polymer in a liquid can be related to the number-average molecular weight of the polymer between cross-links by

$$-\left[\ln(1 - v_2) + v_2 + \chi v_2^2\right] = \left(\frac{V_1}{\bar{v}M_c}\right) \left(1 - \frac{2M_c}{M}\right) \left(v_2^{1/3} - \frac{v_2}{2}\right) \quad (3)$$

where v_2 is the volume fraction of polymer in the swollen polymer in equilibrium with the pure solvent, i.e., v_2 is the reciprocal of the equilibrium value of the swelling index; $v_2 = 1/q$. V_1 is the molar volume of the solvent, \bar{v} is the specific volume of the polymer (reciprocal of its density), M is the molecular weight of the polymer before cross-linking, and M_c is the number-average molecular weight of polymer between cross-linked junctions. χ is a term characterizing the interaction between the solvent and the polymer. χ is negative for good solvents, and incipient precipitation is approached for high-molecular-weight polymers at $\chi = +0.5$. Table 1 lists some χ values for typical polymer-solvent systems.

For typical vulcanized rubbers, q is of the order of 10 in good solvents, and M_c is about 5000. Typical thermoset polymers have M_c much less than 5000, and the swelling equation is not expected to be quantitatively accurate in this case. However, for any given polymer-solvent system, the generalization should still hold that as M_c gets smaller, there is less swelling. Thus, even in highly cross-linked systems, swelling measurements are of value in characterizing the network structure.

Equation (3) can be used to estimate M_c , the number-average molecular weight between cross-links. A possible method of determining the distribution of molecular weights between cross-links is to measure the swelling of a polymer as a function of pressure [4]. The variation of swelling with applied pressure P is

$$-P = \left(\frac{RT}{V_1}\right) \left[\ln(1 - v_2) + v_2 + \chi v_2^2 + \left(\frac{V_1}{\bar{v}M_c}\right) \left(v_2^{1/3} - \frac{v_2}{2}\right)\right] \quad (4)$$

CROSS-LINKING—EFFECT ON PHYSICAL P

Table 1

Polymer-Solvent Interac

| Polymer | Solvent |
|-------------------------|----------------------|
| Polystyrene | Toluene |
| Polystyrene | Methyl ethyl ketone |
| Polyvinyl chloride | Tetrahydrofuran |
| Polyvinyl chloride | Dioxane |
| Polyvinyl chloride | Tributyl phosphat |
| Polyvinyl chloride | Methyl ethyl ketone |
| Natural rubber | Benzene |
| Natural rubber | Carbon tetrachloride |
| Natural rubber | n-hexane |
| Polymethyl methacrylate | Benzene |
| Polymethyl methacrylate | Chloroform |

^a J. Brandrup and E. Immergut, *Polymers*, New York, 1966.

^b G. Bristow and W. Watson, *Trans. Faraday Soc.*, 1966.

However, accurate determinations of M_c by this procedure because of the inherent complexity and the complex mathematical conversion into a distribution function of M_c .

The kinetic theory of rubber [1,5-7] relates the modulus at temperatures well above T_g to the number-average molecular weight between cross-links by

$$G = \left(\frac{r^2}{r_0^2}\right) \frac{dRT}{M_c} \left(1 - \frac{2M_c}{M_n}\right)$$

G is the shear modulus of elasticity, T is the absolute temperature, R is the gas constant, r^2/r_0^2 is the ratio of the square of the distance between network junctions to the square of the distance of network chains in free space, M_n is the number-average molecular weight of un-cross-linked polymer, r^2/r_0^2 is neglected since this ratio is generally fairly well for cross-linked rubbers. Measurements are not slow enough that near equilibrium measurements, especially those on very

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al or sol fraction is defined as

soluble material extractable
total weight of material

izing a cross-linked polymer are
However, in most practical situations
ie cross-linking reactions and their
ily, so all three quantities should be

ked polymer in a liquid can be related
lar weight of the polymer between

$$\frac{V_1}{M_c} \left(1 - \frac{2M_c}{M} \right) \left(v_2^{1/3} - \frac{v_2}{2} \right) \quad (3)$$

n of polymer in the swollen polymer
olvent, i.e., v_2 is the reciprocal of the
ng index; $v_2 = 1/q$. V_1 is the molar
specific volume of the polymer (re-
ac molecular weight of the polymer
s the number-average molecular
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polymer as a function of pressure [4].
applied pressure P is

$$\chi v_2^2 + \left(\frac{V_1}{\bar{v} M_c} \right) \left(v_2^{1/3} - \frac{v_2}{2} \right) \quad (4)$$

CROSS-LINKING-EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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Table 1

Polymer-Solvent Interaction-Parameter χ

| Polymer | Solvent | Temp. (°C) | χ | Ref. |
|-------------------------|----------------------|------------|--------|------|
| Polystyrene | Toluene | 27 | 0.14 | a |
| Polystyrene | Methyl ethyl ketone | 25 | 0.51 | b |
| Polyvinyl chloride | Tetrahydrofuran | 27 | 0.14 | a |
| Polyvinyl chloride | Dioxane | 27 | 0.62 | a |
| Polyvinyl chloride | Tributyl phosphate | 53 | -0.65 | a |
| Polyvinyl chloride | Methyl ethyl ketone | 25 | 0.47 | b |
| Natural rubber | Benzene | 25 | 0.44 | b |
| Natural rubber | Carbon tetrachloride | 20 | 0.28 | a |
| Natural rubber | n-hexane | 25 | 0.43 | b |
| Polymethyl methacrylate | Benzene | 25 | 0.41 | b |
| Polymethyl methacrylate | Chloroform | 25 | 0.33 | b |

^a J. Brandrup and E. Immergut, *Polymer Handbook*, Wiley-Interscience, New York, 1966.

^b G. Bristow and W. Watson, *Trans. Faraday Soc.*, 54, 1742 (1958).

However, accurate determinations of distributions in M_c are difficult by this procedure because of the inherent low sensitivity of Eq. (4) and the complex mathematical conversion of experimental results into a distribution function of M_c .

The kinetic theory of rubber [1,5-7] relates the equilibrium elastic modulus at temperatures well above T_g to the density of cross-links by

$$G = \left(\frac{\bar{r}^2}{\bar{r}_0^2} \right) \frac{dRT}{M_c} \left(1 - \frac{2M_c}{M_n} \right) \quad (5)$$

G is the shear modulus of elasticity, d is the density, T is the absolute temperature, R is the gas constant, M_n is the molecular weight of un-cross-linked polymer, \bar{r}^2/\bar{r}_0^2 is the ratio of the mean-square distance between network junctions to the mean-square end-to-end distance of network chains in free space. The term \bar{r}^2/\bar{r}_0^2 is often neglected since this ratio is generally about 1.0. Equation (5) applies fairly well for cross-linked rubbers if the measurements are carried out slowly enough that near equilibrium is achieved. For fast measurements, especially those on very lightly cross-linked rubbers,

the measured modulus values are greater than those predicted by Eq. (5). At least part of this higher value is due to chain entanglements, which act as temporary cross-links. The term $2M_c/\bar{M}_n$ is a correction for polymer chain ends not effectively tied into the network; if \bar{M}_n is large or if the degree of cross-linking is moderate, this term can be neglected. Equation (5) can also be approximately given by:

$$G \approx \frac{dRT}{M_c} \approx nRT \approx 2C_x RT \approx \frac{\nu RT}{N} \approx 2\rho dRT \quad (6)$$

where n is number of moles of network chains per unit volume of polymer, C_x is the number of moles of tetrafunctional cross-linking agent per unit volume of polymer, ν is the number of cross-linked chains per unit of volume, N is Avogadro's number, and ρ is the number of moles of cross-links per gram of final polymer. This equation implies that

$$n = 2C_x = \frac{d}{M_c} = \frac{\nu}{N} = 2\rho d \quad (7)$$

but Tobolsky [8] suggests that a more accurate equation is

$$n = C_x[2X + 3(1 - X)] \quad (8)$$

where $(1 - X)$ is the mole fraction of cross-linking agent. Around 20°C, the shear modulus is about

$$G \approx 2.5 \times 10^{10} \frac{d}{M_c} \approx 5 \times 10^{10} C_x \quad (9)$$

The effect of very high degrees of cross-linking on elastic modulus is discussed in Sec. IV. Although the kinetic theory of rubber no longer is valid in this case, the elastic modulus still appear to be nearly independent of the chemical structure of the network and to depend primarily upon the tightness of the network structure only. Thus, even at very high degrees of cross-linking, the elastic modulus at high temperatures are still a good empirical method of characterizing cross-linked materials.

Other methods of characterizing network structures discussed in following sections include: the shifting of the glass-transition temperature to higher values (Sec. III), the reduction in the creep of

rubbery materials (Sec. V), and the curing behavior of rubbery polymers (Sec. VI). These methods are largely empirical and relative in nature, but have been made to put the shift in glass-transition temperature on a theoretical foundation. In spite of the lack of a theoretical foundation, these methods are useful because of ease of measurement—especially if the system by other techniques, such as x-ray diffraction.

III. EFFECTS OF CROSS-LINKING

Cross-linking increases the glass-transition temperature of a polymer [9-13]. At low degrees of cross-linking, the shift is very small, but at high degrees of cross-linking, the shift is relative to relatively small changes in M_c . The shift in T_g is not independent of the chemical structure and this is a complicating factor [10]. The cross-linking agent is incorporated into the network, and the chemical composition of the polymer gradient can be considered as a type of cross-linking agent. The shift in the glass-transition temperature is independent effects: (1) the degree of cross-linking, (2) the copolymer effect. The cross-linking agent can be considered as a type of cross-linking agent, while the copolymer effect can either be independent or dependent upon the chemical nature of the copolymer.

A number of studies have been made on the effect of cross-linking on the shift in T_g [9,10,12,13] and agree very well. However, by averaging the data, a shift in T_g of M_c can be made from the shift in

$$T_g - T_{g0} = \frac{3.9 \times 10^4}{M_c}$$

where T_{g0} is the glass-transition temperature of the polymer. It must be remembered that the shift due to cross-linking; the shift in T_g is not accounted for.

DiMarzio [14] and, more recently, from theory an equation relating the shift in T_g to the degree of cross-linking.

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are greater than those predicted by higher value is due to chain entanglement cross-links. The term $2M_c/\bar{M}_n$ is an ends not effectively tied into the the degree of cross-linking is moderate. Equation (5) can also be approxi-

$$RT \approx \frac{\nu RT}{N} \approx 2\nu dRT \quad (6)$$

of network chains per unit volume of moles of tetrafunctional cross-linking agent, ν is the number of cross-linked s Avogadro's number, and ρ is the mass per gram of final polymer. This

$$d \quad (7)$$

a more accurate equation is

$$(8)$$

tion of cross-linking agent. Around out

$$< 10^{10} C_X \quad (9)$$

rees of cross-linking on elastic moduli. Although the kinetic theory of rubber shows that the elastic moduli still appear to be dependent on the chemical structure of the network and to some extent on the density of the network structure only. As the degree of cross-linking, the elastic moduli increase. A good empirical method of character-

izing network structures discussed in the literature is the shifting of the glass-transition temperature. In III, the reduction in the creep of

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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rubbery materials (Sec. V), and the change in the mechanical damping behavior of rubbery polymers (Sec. IV). These methods are largely empirical and relative in nature, although some attempts have been made to put the shift in glass transition on a good theoretical foundation. In spite of the lack of a good theoretical justification, these methods are useful because of their sensitivity and ease of measurement—especially if they are calibrated for each system by other techniques, such as swelling or modulus measurements.

III. EFFECTS OF CROSS-LINKING ON THE GLASS TRANSITION

Cross-linking increases the glass-transition temperature T_g of a polymer [9-13]. At low degrees of cross-linking the shift in T_g is very small, but at high degrees the shift is very large and is sensitive to relatively small changes in M_c . In most systems the shift in T_g is not independent of the chemical composition of the polymer, and this is a complicating factor [10]. As more and more cross-linking agent is incorporated into the network structure, the chemical composition of the polymer gradually changes. The cross-linking agent can be considered as a type of copolymerizing unit. Thus, the shift in the glass-transition temperature is made up of two nearly independent effects: (1) the degree of cross-linking or $1/M_c$ and (2) the copolymer effect. The cross-linking effect always increases T_g and seems to be largely independent of chemical composition, while the copolymer effect can either increase or decrease T_g , depending upon the chemical nature of the cross-linking agent.

A number of studies have been made relating the degree of cross-linking to the shift in T_g [9,10,12,13]. The different studies do not agree very well. However, by averaging the results, rough estimates of M_c can be made from the shift in T_g by the following equation:

$$T_g - T_{g0} = \frac{3.9 \times 10^4}{M_c} \quad (10)$$

where T_{g0} is the glass-transition temperature of the un-cross-linked polymer. It must be remembered that this equation accounts only for the shift due to cross-linking; the shift due to the copolymer effect is not accounted for.

DiMarzio [14] and, more recently, DiBenedetto [15] have derived from theory an equation relating the shift in the glass-transition temperature to the degree of cross-linking. DiBenedetto's equation is

$$\frac{T_g - T_{g^0}}{T_{g^0}} = \frac{\left[\frac{\epsilon_X}{\epsilon_M} - \frac{F_X}{F_M} \right] X_c}{1 - \left(1 - \frac{F_X}{F_M} \right) X_c} \quad (11)$$

where T_{g^0} is the glass-transition temperature of a polymer of the same chemical composition as the cross-linked polymer except the cross-links themselves are absent; the copolymer effect on T_g due to the cross-linking agent is accounted for in T_{g^0} , so Eq. (11) predicts only the shift in T_g due to cross-linking. ϵ_X/ϵ_M is the ratio of the lattice energies for cross-linked and un-cross-linked polymers, while F_X/F_M is the ratio of the segmental mobilities for the same two polymers. X_c is the mole fraction of monomer units which are cross-linked in the polymer. For most polymers it is expected that the mobility of a cross-linked unit is essentially zero, so $F_X/F_M = 0$. The ratio ϵ_X/ϵ_M can be approximated by

$$\frac{\epsilon_X}{\epsilon_M} \approx \frac{d_M}{d_X} \frac{(M_0)_X}{(M_0)_M} \left(\frac{\delta_X}{\delta_M} \right)^2 \quad (12)$$

where the d 's are the densities of the cross-linked and un-cross-linked polymers, $(M_0)_M$ is the molecular weight of an un-cross-linked monomer unit, $(M_0)_X$ is the molecular weight of a cross-linked monomer unit, while δ_X and δ_M are the solubility parameters of cross-linked and un-cross-linked polymer, respectively. DiBenedetto [15] has estimated that $\epsilon_X/\epsilon_M \approx 1.2$ for the styrene-divinylbenzene system, and a similar value should hold for many other cross-linked systems. Equation (11) can be approximately given in such cases, by

$$\frac{T_g - T_{g^0}}{T_{g^0}} \approx \frac{1.2 X_c}{1 - X_c} \quad (13)$$

At low concentrations of cross-linking agent,

$$\frac{X_c}{1 - X_c} \approx \frac{2}{n_c} \quad (14)$$

Thus, from Eqs. (11), (12), and (14),

$$T_g - T_{g^0} = \frac{2 d_M (M_0)_X}{d_X (M_0)_M} \left(\frac{\delta_X}{\delta_M} \right)^2 \frac{T_{g^0}}{n_c} \approx \frac{2 T_{g^0}}{n_c} \quad (15)$$

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The theoretical Eq. (15) has essentially the same form as the empirical Eq. (10). However, Eq. (15) does not depend on the nature of the polymer. The part depending on the nature of the polymer is the factor n_c , which is roughly 1.0 or a little greater, in most cases. In fact, Eq. (15) has the same form as a

$$T_g - T_{g^0} \approx \frac{780}{n_c}$$

where n_c is the average number of cross-links between cross-links. There are not enough data available to decide with any degree of accuracy; however, Eqs. (13) and (15) are empirical equations.

IV. EFFECT OF CROSS-LINKING ON PHYSICAL PROPERTIES AND UPON

Typical dynamic mechanical behavior of temperature is illustrated in Fig. 1. The damping peak, say one cycle per second or less, shifts to higher temperatures as the cross-linking increases. The damping peak at the glass transition. The damping peak shifts to higher temperatures as the cross-linking increases. The damping peak shifts to higher temperatures as the cross-linking increases.

Typical data on a highly cross-linked formaldehyde plastics are given in Fig. 2. It is seen that cross-linking has little effect on the glass transition temperature, T_g , i.e., at temperatures well below T_g the material is rigid. However, at T_g , the modulus is strongly dependent on cross-linking. The increase in modulus is predicted by the kinetic theory of rubber elasticity.

In addition to the changes in modulus, the damping peak (which is in the transition region) is shifted to higher temperatures as cross-linking increases. This broadening is inherently due to cross-linking in the cross-linked structure. The distribution in the lengths of chains between cross-links would remain fairly sharp as long as the cross-linking is not too high. In some highly cross-linked systems

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$$\frac{x_c}{x_c} \quad (11)$$

ion temperature of a polymer of the the cross-linked polymer except the sent; the copolymer effect on T_g due counted for in T_{g0} , so Eq. (11) pre- cross-linking. ϵ_x/ϵ_M is the ratio of linked and un-cross-linked polymers, segmental mobilities for the same fraction of monomer units which are for most polymers it is expected that unit is essentially zero, so $F_x/F_M = 0$. mated by

(12)

of the cross-linked and un-cross- molecular weight of an un-cross- he molecular weight of a cross- and δ_M are the solubility parameters inked polymer, respectively. DiBene- $\epsilon/\epsilon_M = 1.2$ for the styrene-divinyl value should hold for many other n (11) can be approximately given in

(13)

linking agent,

(14)

(14),

$$\left(\frac{x_c}{x_M}\right)^2 \frac{T_{g0}}{n_c} \approx \frac{2T_{g0}}{n_c} \quad (15)$$

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES OF POLYMERS 79

The theoretical Eq. (15) has essentially the same form as the empirical Eq. (10). However, Eq. (15) does depend somewhat on the structure of the polymer. The part depending upon the ratios of densities, monomer molecular weights, and solubility parameters should be roughly 1.0 or a little greater, in many cases. Except for the term T_{g0} , Eq. (15) has the same form as another empirical equation [13]:

$$T_R - T_{R0} \approx \frac{788}{n_c} \quad (16)$$

where n_c is the average number of atoms in the polymer backbone between cross-links. There are not enough good experimental data available to decide with any degree of confidence which equation is best; however, Eqs. (13) and (15) are probably preferable to the empirical equations.

IV. EFFECT OF CROSS-LINKING ON DYNAMIC MECHANICAL PROPERTIES AND UPON ELASTIC MODULI

Typical dynamic mechanical behavior of polymers as a function of temperature is illustrated in Fig. 2. At low frequencies of vibration, say one cycle per second or less, the damping peak and the drastic drop in the modulus occur at about the same temperature as the glass transition. The damping peak is shifted to higher temperatures as the test frequency is increased; typical results are about 7°C shift for each factor-of-ten increase in the frequency [16].

Typical data on a highly cross-linked material such as phenol-formaldehyde plastics are given in Fig. 3 [11]. These results show that cross-linking has little effect on the modulus of a polymer below T_g , i.e., at temperatures well below the damping peak, where the material is rigid. However, at temperatures above the damping peak, the modulus is strongly dependent upon the extent of cross-linking. The increase in modulus is much more than what would be predicted by the kinetic theory of rubber.

In addition to the changes in modulus at high temperatures, Fig. 3 shows that the damping peak (which is associated with the glass-transition region) is shifted to higher temperatures and is greatly broadened as cross-linking increases. It is not known whether this broadening is inherently due to cross-linking or if it is due to heterogeneity in the cross-linked structure. Possibly, if there were no distribution in the lengths of chains between cross-links, the transition region would remain fairly sharp as it does in a linear polymer [9]. In some highly cross-linked systems the transition region is so

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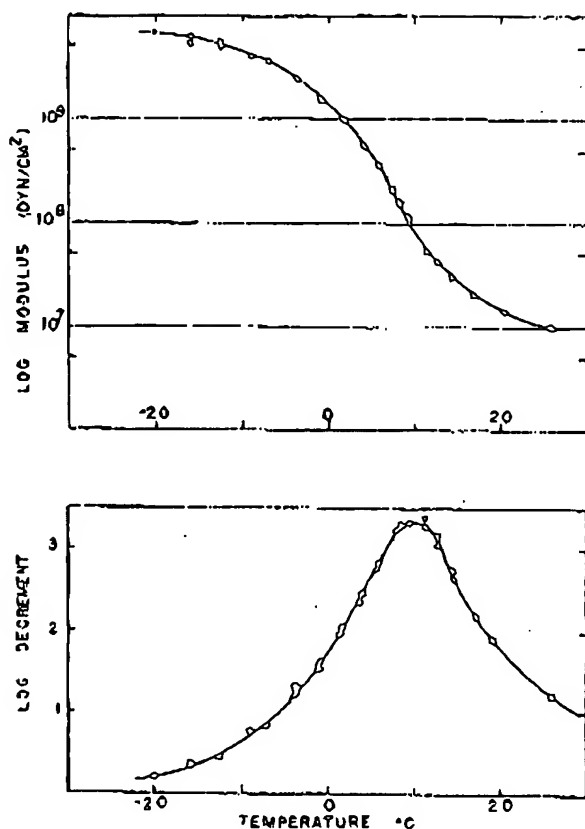


Fig. 2. Typical dynamic mechanical properties of an un-cross-linked polymer. Upper curve is the logarithm of the shear modulus. Lower curve is the mechanical damping (logarithmic decrement). [Reprinted from *Rev. Sci. Instr.*, 22, 690 (1951).]

CROSS-LINKING-EFFECT ON PHYSICAL P

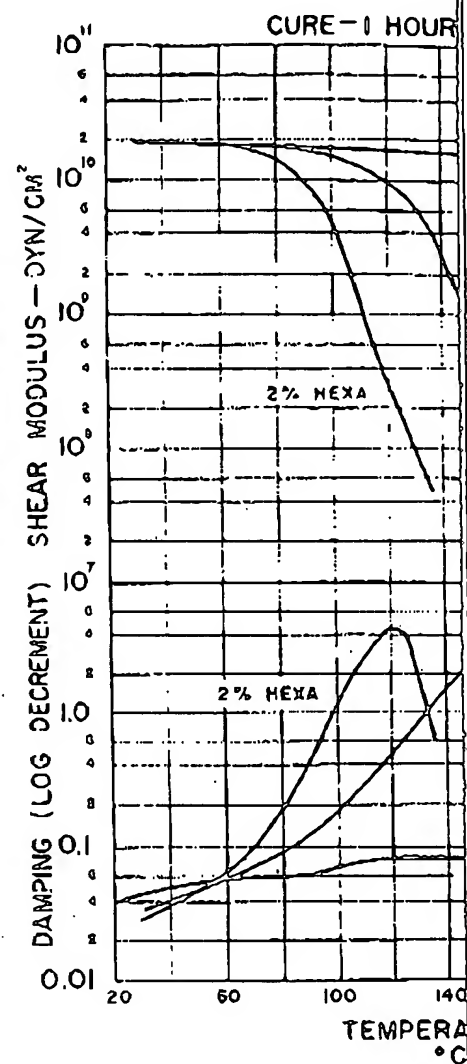
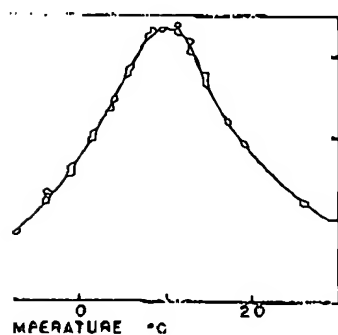
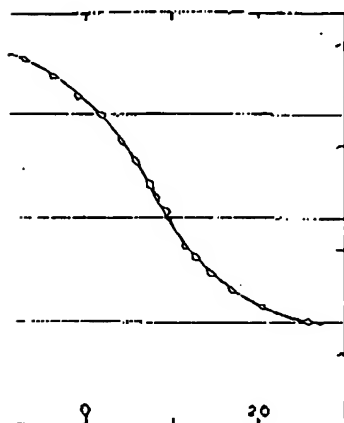


Fig. 3. Dynamic mechanical properties of a (novolac) cross-linked with various amounts (hexa). [Reprinted from *Ind. Eng. Chem.*, 4, the copy owner, The American Chemical Society.]

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1) properties of an un-cross-linked polymer of the shear modulus. Lower curve is the log decrement. [Reprinted from Rev.

CROSS-LINKING-EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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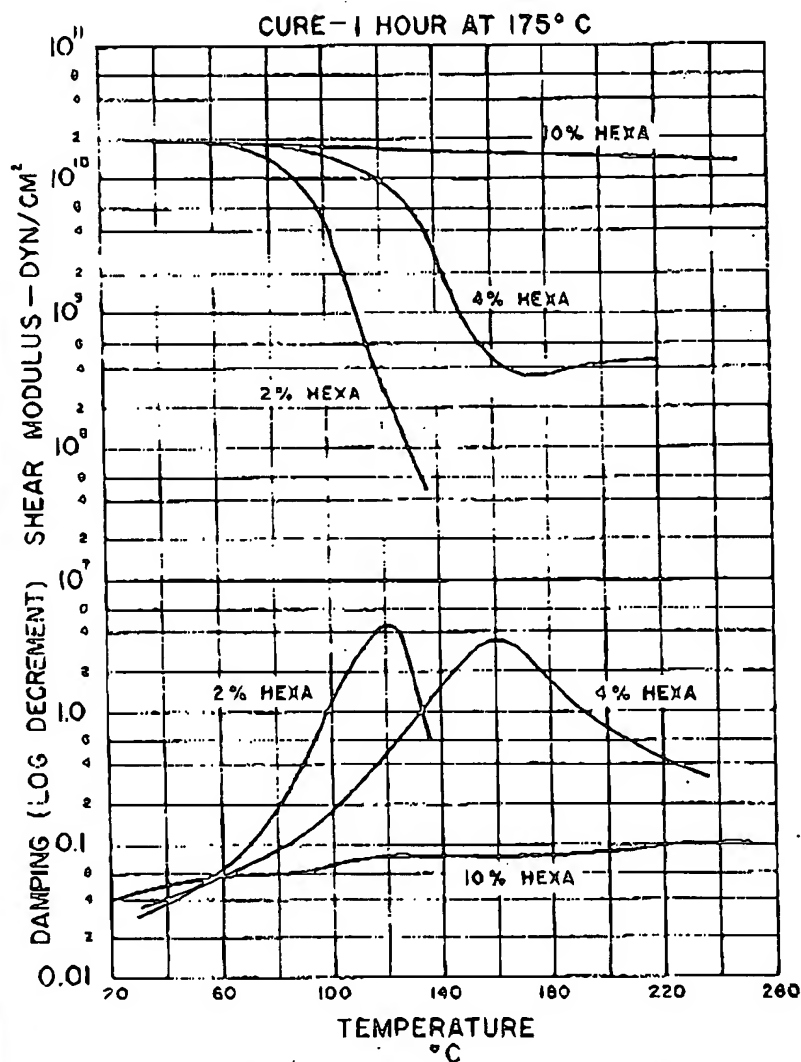


Fig. 3. Dynamic mechanical properties of a phenol-formaldehyde resin (novolac) cross-linked with various amounts of hexamethylenetetramine (hexa). [Reprinted from *Ind. Eng. Chem.*, 48, 76 (1956) with permission of the copy owner, The American Chemical Society.]

broadened and shifted to such high temperatures, that it is impossible to tell whether a glass transition actually exists before decomposition takes place to obscure the experimental results.

Dynamic mechanical tests are a rapid and very sensitive measure of cross-linking at temperatures above T_g . The kinetic theory of rubber shows that the modulus can be used to measure cross-linking, but for lightly cross-linked rubbers, the mechanical damping may be a much more sensitive indicator of cross-linking [17,18]. In the present state of the art, damping is a relative, not an absolute, method of measuring cross-linking. However, when it is calibrated for a given system, damping is a rapid and sensitive method of measuring M_c . Figure 4 shows how the damping differs for a very lightly vulcanized rubber and a highly cross-linked rubber [18]. In many respects, the damping of a very lightly cross-linked rubber resembles that of a non-cross-linked polymer. The reasons for this are not clearly understood, but it is believed to be related to trapped entanglements [19]. Figure 5 is a calibration curve relating damping above T_g to the swelling of a rubber in a good solvent. Damping decreases as M_c decreases. This would be expected if one assumes that a perfectly elastic system should not dissipate any energy as heat, i.e., its damping should be zero. The mechanical damping is a very convenient method of measuring the degree of cross-linking of rubbers since it requires only a few minutes; swelling measurements generally require several days.

At very high degrees of cross-linking that are characteristic of thermoset polymers, rubber theory no longer is applicable, and Eq. (5) is not valid at moduli much greater than 10^8 dyn/cm². An empirical approach such as that used by Tobolsky [8,20-23] is then needed to relate elastic moduli to degree of cross-linking. Fortunately, a unique relationship seems to hold which is nearly independent of the chemical composition of the polymer as long as the modulus is measured at temperatures well above the glass-transition temperature. This effect of high degrees of cross-linking on modulus is illustrated in Fig. 6 for a series of polyethyl acrylate-tetraethylene glycol dimethacrylate (TEGDM) copolymers in which the TEGDM acts as a cross-linking agent [22]. An equation that appears to give a reasonable estimate of the degree of cross-linking for highly cross-linked polymers is

$$\log_{10} G \approx 7.0 + \frac{293d}{M_c} \approx 7.0 + 585 C_x \quad (17)$$

CROSS-LINKING—EFFECT ON PHYSICAL

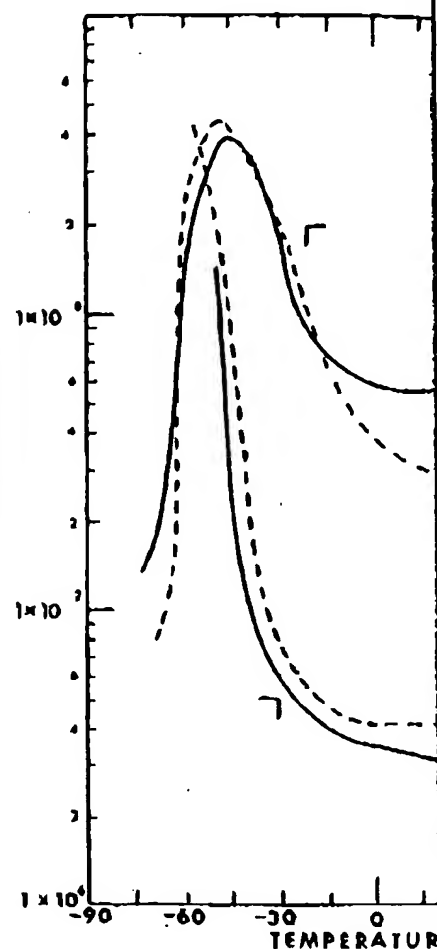


Fig. 4. Dynamic mechanical properties of lightly cross-linked rubber, $q = 1$ sol fraction = 3.8%, $q = 6.5$, sol fraction = 3.8%. Note is shear modulus in dyn/cm². [Reprint 8, 611 (1964).]

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high temperatures, that it is impossible to actually exist before decomposition. Experimental results.

are a rapid and very sensitive measure of cross-linking above T_g . The kinetic theory of cross-linking can be used to measure cross-linking. However, the mechanical damping may be used for or of cross-linking [17,18]. In the case of cross-linking is a relative, not an absolute, measure. However, when it is calibrated with a rapid and sensitive method of measurement the damping differs for a very lightly cross-linked rubber [18]. In many cases a lightly cross-linked rubber resembles a polymer. The reasons for this are not understood to be related to trapped energy in a calibration curve relating damping of rubber in a good solvent. Damping decreases would be expected if one assumes that energy should not dissipate any energy as it approaches zero. The mechanical damping is a measure of the degree of cross-linking in a few minutes; swelling measurements take days.

Cross-linking that are characteristic of a theory no longer is applicable, and much greater than 10^6 dyn/cm². An equation used by Tobolsky [8,20-23] is then used to degree of cross-linking. Fortunately it holds which is nearly independent of the polymer as long as the temperatures well above the glass-transition of high degrees of cross-linking on 6 for a series of polyethyl acrylate-acrylate (TEGDM) copolymers in which cross-linking agent [22]. An equation that estimates the degree of cross-linking is

$$7.0 + 585 C_x \quad (17)$$

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES OF POLYMERS 83

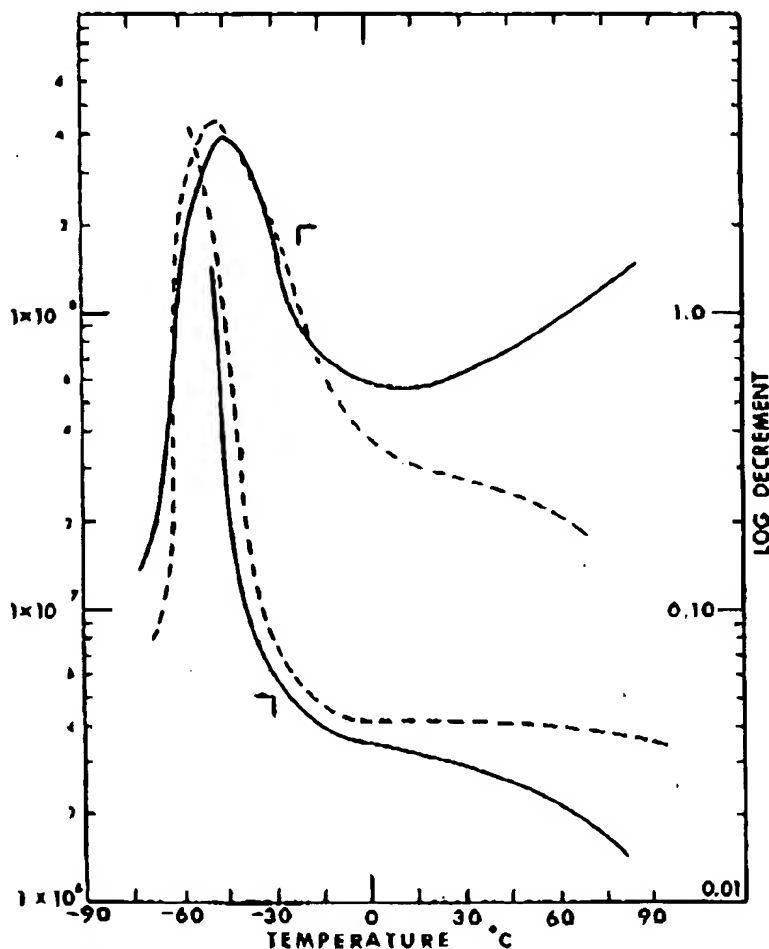


Fig. 4. Dynamic mechanical properties of butyl rubbers: (—) very lightly cross-linked rubber, $q \approx \infty$ sol fraction ≈ 1 ; (----) highly cross-linked rubber, $q = 6.5$, sol fraction $\approx 3.8\%$, $M_c \approx 11,000$. The left-hand ordinate is shear modulus in dyn/cm². (Reprinted from *J. Appl. Polymer Sci.*, 8, 511 (1964).)

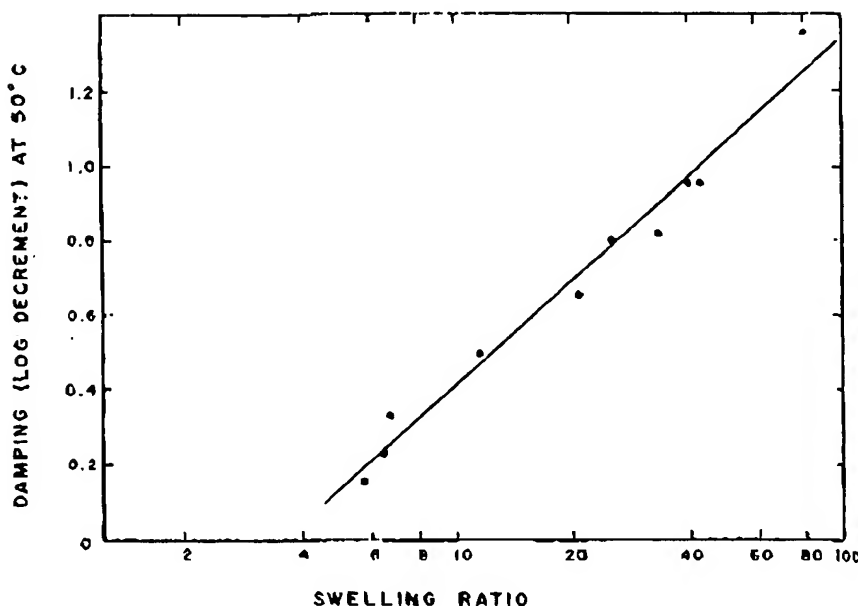


Fig. 5. Relation of mechanical damping at 50°C to the swelling ratio q for cross-linked SBR rubber. The solvent is benzene for the swelling test.

The equation holds at temperatures that are about 30°C above T_g (or higher). Its valid range is believed to be roughly 2×10^7 to at least 2×10^9 dyn/cm². Figure 7 shows that in the range of shear moduli from 10^7 to 10^9 dyn/cm², Eq. (17) and the kinetic theory of rubber give comparable values. At higher degrees of cross-linking, the kinetic theory gives values which are too low. Equation (17) is, at best, a rather crude empirical relationship, but better experimental data or advances in our theoretical knowledge are required to improve upon it.

Generally, the glass transition of a cross-linked polymer will not go much higher than the curing temperature or the temperature at which the polymer was formed, even if the T_g would be expected to be much higher [11,24]. This is because most chemical reactions essentially stop at temperatures below T_g . Thus, most cross-linking reactions stop when the reaction has proceeded to the point where T_g

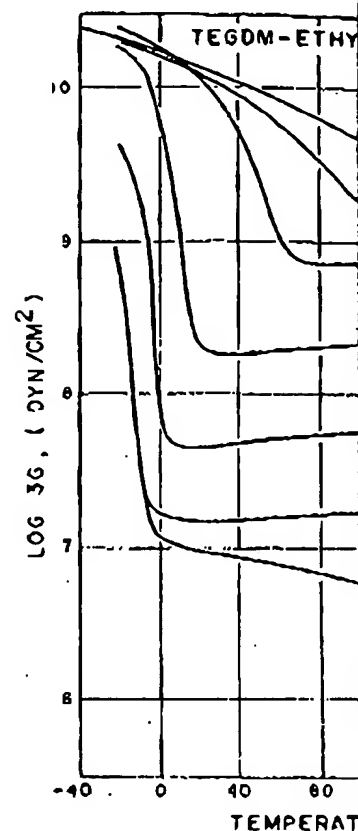
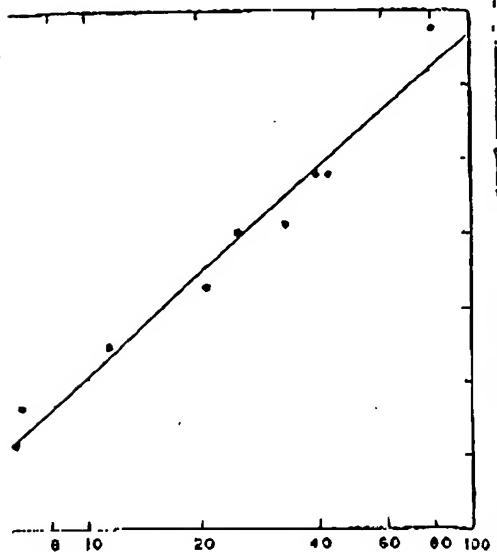


Fig. 6. Young's modulus (or $3 \times$ shear modulus) for ethyl acrylate copolymers cross-linked with tetraethylene glycol dimethacrylate (TEGDMA) from Tobolsky, et al., *J. Polymer Sci.*, 2.

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Sampling at 50°C to the swelling ratio q for solvent is benzene for the swelling test.

temperatures that are about 30°C above T_g is believed to be roughly 2×10^7 to at 7 shows that in the range of shear m^2 , Eq. (17) and the kinetic theory of es. At higher degrees of cross-linking, is which are too low. Equation (17) is, ical relationship, but better experi-ur theoretical knowledge are required

tion of a cross-linked polymer will during temperature or the temperature med, even if the T_g would be expected his is because most chemical reactions res below T_g . Thus, most cross-linking tion has proceeded to the point where T_g

CROSS-LINKING-EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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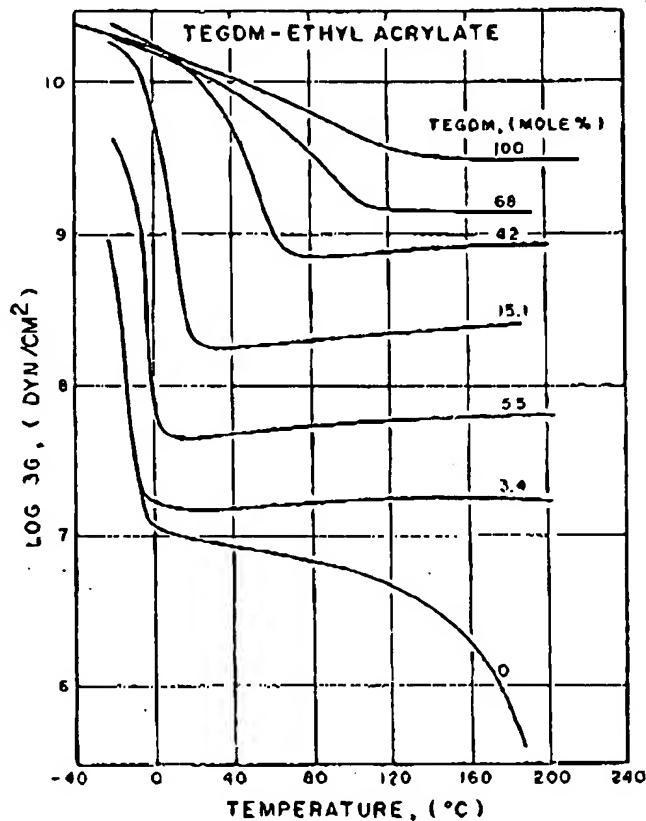


Fig. 6. Young's modulus (for $3 \times$ shear modulus G) as a function of temperature for ethyl acrylate copolymers cross-linked to various degrees with tetraethylene glycol dimethacrylate (TEGDM) co-monomer. (Reprinted from Tobolsky, et al., *J. Polymer Sci.*, 2A, 2749 (1964).)

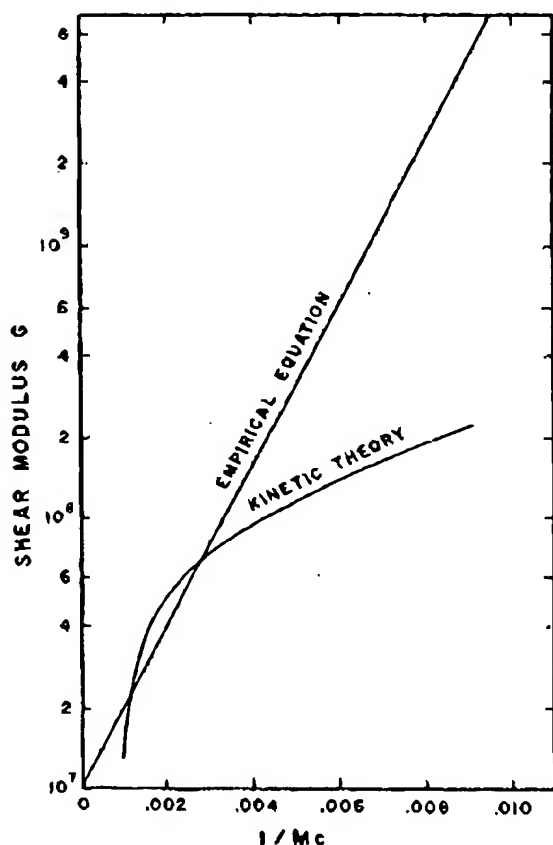


Fig. 7. Logarithm of the shear modulus above the glass-transition temperature as a function of the degree of cross-linking $1/M_c$ according to an empirical correlation. The predicted modulus according to the kinetic theory of rubber is given for comparison.

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES

is raised to the temperature at which it softens. If the temperature is further raised, the modulus continues to decrease and can be detected by modulus measurements. The modulus as a function of temperature decreases near T_g . If further reaction occurs, the modulus soon starts to increase rather than to decrease as the temperature is raised. Thus, dynamic mechanical tests are useful in studying the extent of cross-linking as a function of time and temperature.

Recent theoretical [25] and experimental work indicates that the network structure of many cross-linked epoxy resins is not the simple homogeneous network. Rather, the polymer can consist of high modulus regions or particles embedded in a less highly cross-linked matrix. This two-phase network structure can be seen by electron microscopy, also by dynamic mechanical tests. Figure 8 shows the behavior of a two-phase epoxy resin with a high modulus phase. The behavior is similar over-all chemical composition and the matrix phase clearly shows up as a damping curve, while the homogeneous phase shows a much lower peak.

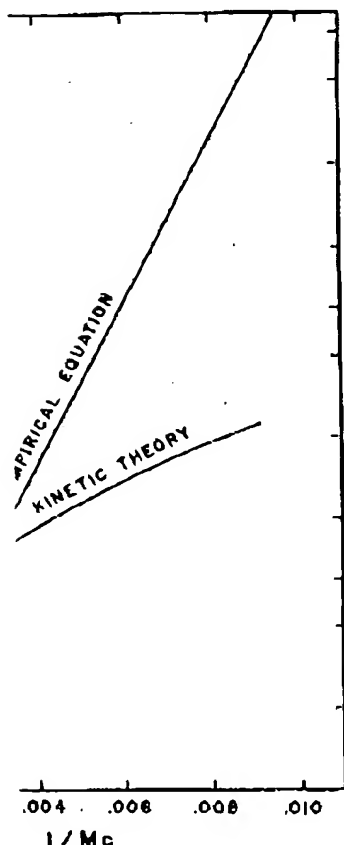
V. CREEP

In creep tests the elongation or deformation is measured as a function of time under a constant load. It is well known that cross-linking greatly reduces creep in a rubbery material, but surprisingly little is known about the effect of cross-links in view of the great practical importance of creep. The effect of cross-links is especially pronounced in short times creep, since cross-linking has a much stronger effect on rubbers, since entanglements can act as temporary cross-links, decreasing the elongation. Figure 9 illustrates the sensitivity of creep to the extent of cross-linking. Even very small degrees of cross-linking reduce creep. The creep rate decreases with time, but even with rubbers of very low swelling, creep goes on forever at a slow rate [27,28]. It is expected that creep should be proportional to the 5/3 power of the swelling, which has been accurately experimentally and should be used as an approximation.

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modulus above the glass-transition temperature of cross-linking $1/M_c$ according to an empirical modulus according to the kinetic theory of

is raised to the temperature at which the reaction is being carried out. If the temperature is further raised, the reaction can again continue and can be detected by modulus measurements. In measuring the modulus as a function of temperature, the modulus will decrease near T_g . If further reaction takes place, the modulus will soon start to increase rather than to decrease (as it normally does) as the temperature is raised. Thus, dynamic mechanical tests are useful in studying the extent of cross-linking reactions as functions of time and temperature.

Recent theoretical [25] and experimental [24,26] results indicate that the network structure of many cross-linked polymers such as epoxy resins is not the simple homogeneous type generally assumed. Rather, the polymer can consist of highly cross-linked micro-gel particles embedded in a less highly cross-linked matrix. This two-phase network structure can be seen by microscopic techniques and also by dynamic mechanical tests. Figure 8 compares the damping behavior of a two-phase epoxy resin with a homogeneous polymer of similar over-all chemical composition [24]. The micro-gel phase and the matrix phase clearly show up as two peaks in the broad damping curve, while the homogeneous polymer has a single narrower peak.

V. CREEP

In creep tests the elongation or deformation of a specimen is measured as a function of time under the action of a constant load. It is well known that cross-linking greatly reduces the creep of a rubbery material, but surprisingly little quantitative data are available, in view of the great practical importance of the subject. The effect of cross-links is especially pronounced at long times; at very short times cross-linking has a much smaller effect on the creep of rubbers, since entanglements can act as temporary cross-links in decreasing the elongation. Figure 9 illustrates the tremendous sensitivity of creep to the extent of cross-linking as measured by swelling ratio and sol fraction [18]. Even very imperfect network structures with low degrees of cross-linking and high sol fractions greatly reduce creep. The creep rate decreases as cross-linking increases, but even with rubbers of very low swelling ratio, creep appears to go on forever at a slow rate [27,28]. From theory it might be expected that creep should be proportional to $q^{1/3}$ [1]. This dependence of creep on the $5/3$ power of the swelling ratio is not found to hold accurately experimentally and should be considered as only a first approximation.

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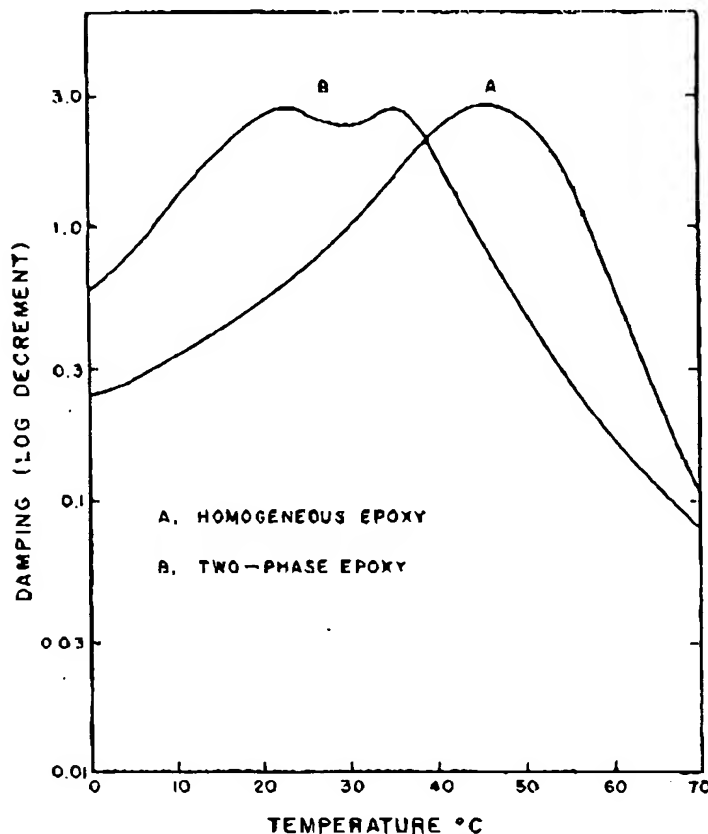


Fig. 8. Comparison of the damping of a homogeneous epoxy resin (A) with a heterogeneous epoxy containing micro-gel (B) of a similar chemical composition.

Plazek [29] has carried out very accurate creep work on natural rubber as a function of cross-linking. In addition to the general effects discussed above, he found that for a given degree of cross-linking, data at different temperatures could be superimposed by the usual W-L-F shift factors which were developed for non-cross-linked polymers [30]. Furthermore, curves for different degrees of cross-

CROSS-LINKING-EFFECT ON PHYSICAL

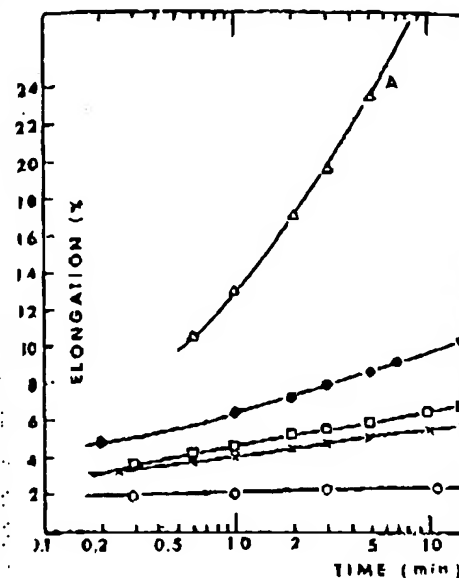


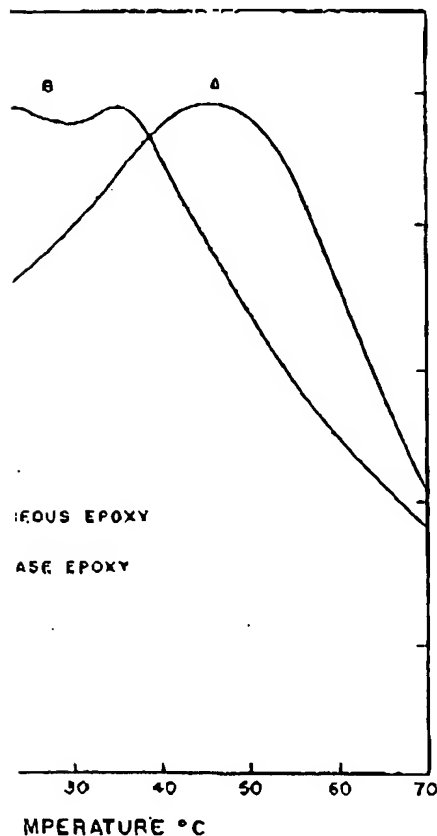
Fig. 9. Creep of SBR rubbers at 24°C: (A) lightly cross-linked rubber, $M_c \approx 29$; (C) moderately cross-linked rubber, $M_c \approx 100$; (D) moderately cross-linked rubber, $M_c \approx 100$; (F) highly cross-linked rubber, $M_c \approx 320$. Load = 5 lb/in². [Reprinted from *J. Appl. Phys.*]

linking could be superimposed to give zontal and vertical shifts of the creep given by

$$\log \left(\frac{E_e(M_c)}{E_e(M_c^0)} \right)$$

where $E_e(M_c)$ is the long-time equilibrium modulus of a reference represented by M_c^0 . The horizontal shift function of the degree of cross-linking

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ping of a homogeneous epoxy resin (A) with a micro-gel (B) of a similar chemical compo-

out very accurate creep work on natural is-linking. In addition to the general found that for a given degree of cross-temperatures could be superimposed by the which were developed for non-cross-linked ce, curves for different degrees of cross-

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES OF POLYMERS

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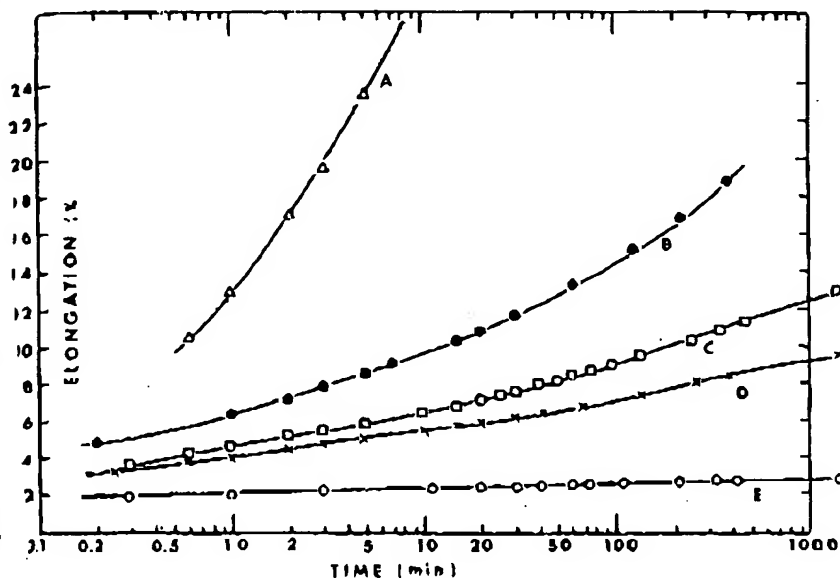


Fig. 9. Creep of SBR rubbers at 24°C: (A) un-cross-linked, $M_v = 280,000$; (B) lightly cross-linked rubber, $M_c \approx 29,000$, $q = 33.5$, sol fraction = 34%; (C) moderately cross-linked rubber, $M_c \approx 18,200$, $q = 25.8$, sol fraction = 24%; (D) moderately cross-linked rubber, $M_c \approx 14,400$, $q = 21$, sol fraction = 20.4%; (E) highly cross-linked rubber, $M_c \approx 5200$, $q = 6.8$, sol fraction = 9.5%. Load = 5 lb/in². [Reprinted from *J. Appl. Polymer Sci.*, 8, 611 (1964).]

linking could be superimposed to give a master creep curve by horizontal and vertical shifts of the creep curves. The vertical shift is given by

$$\log \left(\frac{E_c(M_c)}{E_c(M_c^0)} \right)$$

where $E_c(M_c)$ is the long-time equilibrium modulus of a rubber with a degree of cross-linking corresponding to M_c , while $E_c(M_c^0)$ is the equilibrium modulus of a reference rubber with cross-linking represented by M_c^0 . The horizontal shift along the time axis is also a function of the degree of cross-linking.

Although many creep measurements have been made on cross-linked polymers in the glassy state, these creep tests have generally been of an engineering nature, and little of scientific value can be obtained from them. The degree of cross-linking has been unknown, and the effects of cross-linking have been obscured by the presence of fillers. However, it appears that cross-linking has no major effect on creep of polymers at temperatures well below their glass-transition region. In rigid brittle polymers, molecular motions are so frozen in, that the additional restrictions of cross-links are hardly noticeable. However, at high loads, at very long times, or at temperatures not far below T_g , cross-linking should reduce creep.

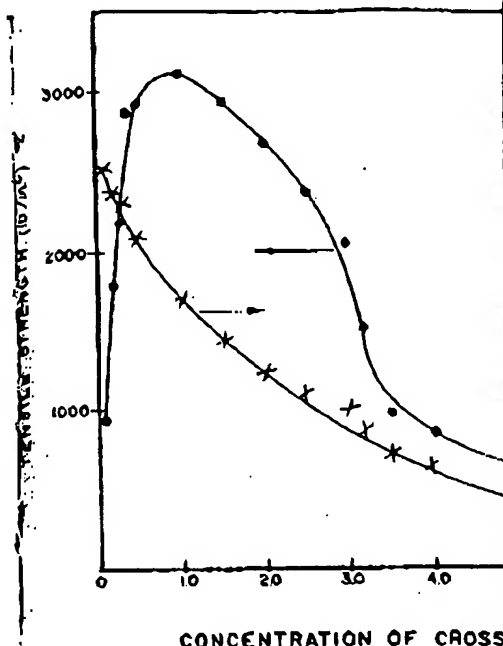
The creep of rigid polymers is strongly dependent upon the elastic modulus of the polymer, the mechanical damping, and the difference between T_g and the ambient temperature. Some thermoset materials such as phenol-formaldehyde and melamine resins have high moduli, low mechanical damping, and high glass-transition temperatures. All of these factors tend to reduce creep and creep rate, so these types of polymers generally have low creep and very good dimensional stability. On the other hand, some epoxy and polyester resins have much greater creep; they often have shear moduli less than 10^{10} dyn/cm² because of low-temperature, secondary glass transitions. In addition, because of their chemical structure and low curing temperatures, many epoxy resins have relatively low glass-transition temperatures. For these reasons, typical epoxy resins may have considerably greater creep than the more highly cross-linked phenol-formaldehyde resins.

VI. STRESS-STRAIN BEHAVIOR

The effect of cross-linking on stress-strain properties of rubbers and polymers above their glass-transition temperatures is well established. However, at temperatures below T_g , little is known, and the evidence is somewhat contradictory.

Many examples of polymers above their T_g have been shown to follow the same general trends illustrated in Fig. 10 [31-35]. The elongation to break ϵ_b decreases as cross-linking increases. $\epsilon_b = (\lambda_b - 1)$, where λ_b is the extension ratio at break. The tensile strength first increases with cross-linking, goes through a maximum at low degrees of cross-linking, and then progressively decreases. Theory suggests that the extension ratio to break λ_b should be proportional to the square root of the reciprocal of the density of effective cross-links ν_e [32,36]. Experimentally, it has been found in some cases, that indeed $\lambda_b \propto 1/\nu_e^{1/2}$, [37], but in other cases, the

CROSS-LINKING—EFFECT ON PHYSICAL PROPERTIES



CONCENTRATION OF CROSS

Fig. 10. Stress-strain properties of rubber cross-linking agent. [From the data of J. P.

relation is not accurately followed. Th up to the maximum value the tensile st tional to $\nu_e^{1/2}$ or to ν_c . Experimentally correct, but some experimental data of portional to $\nu_e^{1/2}$ rather than to $\nu_c^{1/2}$ or

Although the stress-strain behavior variation with cross-linking, these me be expected to reveal other factors cha ture. Network structures are not perfe tive intramolecular cross-links in the branches. Loops become especially nu reaction is carried out in the presence loops manifest themselves during mecl

Measurements have been made on cross-linked state, these creep tests have generally little scientific value can be given. Degree of cross-linking has been unknown, and have been obscured by the presence of factors that cross-linking has no major effect on properties at temperatures well below their glass-transition temperatures. For polymers, molecular motions are so restricted that cross-links are hardly broken under loads, at very long times, or at temperatures above their glass-transition temperatures. Creep is strongly dependent upon the elastic modulus, mechanical damping, and the difference between the operating and the glass-transition temperature. Some thermoset materials such as melamine resins have high moduli, high glass-transition temperatures. All these factors reduce creep, so these types of polymers show low creep and very good dimensional stability. Some epoxy and polyester resins have low modulus and low glass-transition temperatures, secondary glass transitions. In chemical structure and low curing temperatures, typical epoxy resins may have comparable creep to the more highly cross-linked phenol-

STRESS-STRAIN BEHAVIOR

On stress-strain properties of rubbers at temperatures below T_g , little is known, and the data are contradictory.

Above their T_g have been shown to be as illustrated in Fig. 10 [31-35]. The properties change as cross-linking increases.

The extension ratio at break. The tensile strength, goes through a maximum with increasing cross-linking, and then progressively decreases. The extension ratio to break λ_b should be proportional to the reciprocal of the density of effective cross-links. Experimentally, it has been found in $1/\nu_c^{1/2}$ [37], but in other cases, the

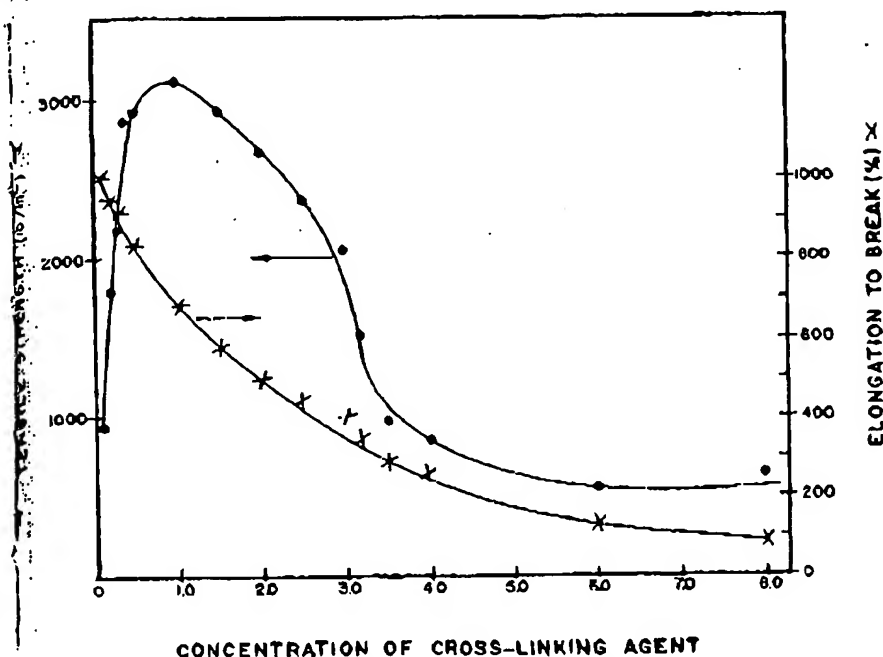


Fig. 10. Stress-strain properties of rubber as a function of the percent of cross-linking agent. [From the data of *J. Polymer Sci.*, 4, 485 (1949).]

relation is not accurately followed. Theories [32,38,39] predict that up to the maximum value the tensile strength σ_b should be proportional to $\nu_c^{1/2}$ or to ν_c . Experimentally, this is found to be roughly correct, but some experimental data on tensile strength may be proportional to $\nu_c^{1/2}$ rather than to $\nu_c^{1/2}$ or ν_c [40].

Although the stress-strain behavior of rubbers shows pronounced variation with cross-linking, these mechanical properties would also be expected to reveal other factors characterizing the network structure. Network structures are not perfect and contain many ineffective intramolecular cross-links in the form of polymer loops or branches. Loops become especially numerous if the cross-linking reaction is carried out in the presence of an inert diluent. These loops manifest themselves during mechanical tests by decreased

modulus and strength [41]. Case [42] has developed a theory which predicts how other network characteristics should affect stress-strain properties. This theory indicates that rubbers containing trifunctional branched cross-links should have greater elongations to break than equivalent rubbers containing tetrafunctional cross-links. The theory also predicts that rubbers with regularly spaced cross-links should have greater elongations to break than rubbers containing randomly spaced branch points. Although intramolecular loops are ineffective in carrying an applied load, interpenetrating loops, on the other hand, can increase the number of effective cross-link points and can help carry an applied load [43].

Smith [44,45] has proposed the "failure envelope" as a convenient way of compressing a great deal of stress-strain data into a single diagram. A typical fracture envelope is illustrated in Fig. 11 [45]. In such a diagram the logarithm of the tensile strength is plotted against the logarithm of the elongation to break. The failure envelope

FRACTURE ENVELOPE FOR SBR VULCANIZATE

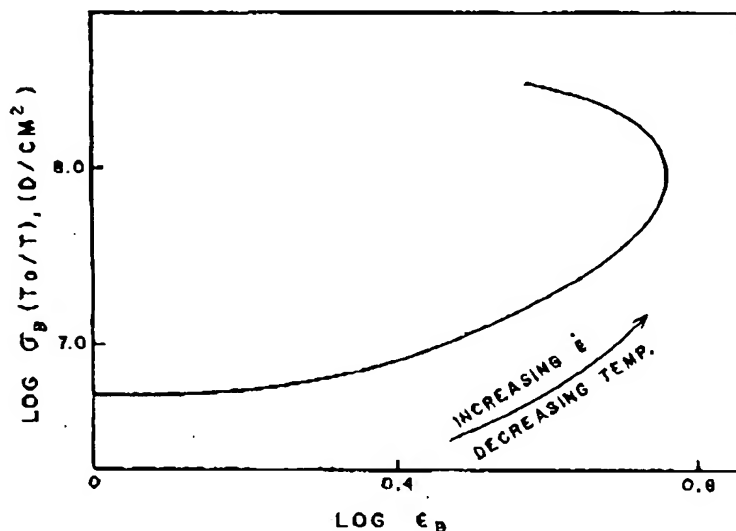


Fig. 11. Failure envelope for SBR vulcanizate, a typical polymer. (Reprinted with modifications from *J. Polymer Sci.*, 1A, 3597 (1963).)

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is nearly independent of the temperature. The curves are reduced to a common reference temperature by multiplying the tensile strength by T_0/T , once temperature to the actual temperature. Lowering the temperature or increasing the time for the test (decreasing the time for the test) moves the curve in a counterclockwise direction around the origin. In the rubbery state are at the bottom hand side, while rigid polymers are at the top. The failure envelope is calculated on the basis of the original area at point of fracture, obtained in constant-load-creep rupture stress-strain tests.

Figure 12 illustrates the effect of cross-linking on the failure envelopes. As expected from the theory, cross-linking shifts the envelope up and to the left. The degree of cross-linking in the rubbery state is taken care of the necessary vertical shift. The curves for different degrees of cross-linking are shifted to give a single curve [37]. The master curves for all degrees of cross-linking are plotted against $\log E_e \epsilon_B (T_0/T)$ where E_e is the modulus of the rubber [45].

Unambiguous data on the effect of cross-linking on the strain properties of rigid polymers is scarce. In most cases, changing the degree of cross-linking has little effect. For long-chain rigid polymers such as polystyrene, cross-linking may increase the tensile strength but also makes the polymer very brittle. For example, with styrene-butadiene, the tensile strength increases with cross-linking to 7400 psi at 4% divinylbenzene, then drastically decreases to 1000 psi at 8% divinylbenzene. Theoretically, one would expect tensile strength to increase with cross-linking because weak Van der Waals bonds are replaced by strong covalent bonds. The decrease in tensile strength is due to submicroscopic cracks develop which result from shrinkage or thermal degradation of molecular segments has been deduced.

For thermoset polymers such as epoxies, the tensile strength rapidly increases (or cures). Such low-molecular-weight

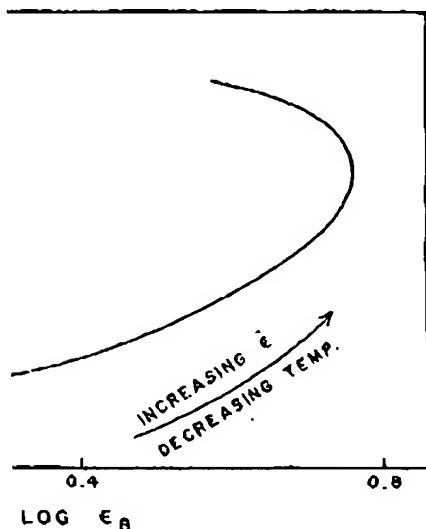
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Case [42] has developed a theory which indicates that rubbers containing tri- and tetrafunctional cross-links should have greater elongations to break than rubbers containing regularly spaced cross-links. Although intramolecular loops and interpenetrating loops, under applied load, increase the number of effective cross-links, the failure envelope as a convenient method of stress-strain data into a single envelope is illustrated in Fig. 11 [45]. The tensile strength is plotted against elongation to break. The failure envelope

FAILURE ENVELOPE FOR SBR VULCANIZATE



R vulcanizate—a typical polymer. [Reprinted from *Ind. Eng. Chem. Anal. Ed.*, 1A, 3597 (1963).]

is nearly independent of the temperature or rate of testing, if the curves are reduced to a common reference temperature by multiplying the tensile strength by T_0/T , i.e., by the ratio of the reference temperature to the actual temperature, both in degrees Kelvin. Lowering the temperature or increasing the rate of testing (decreasing the time for the test) moves the experimental data in a counterclockwise direction around the failure envelope. Polymers in the rubbery state are at the bottom of the diagram or to the right-hand side, while rigid polymers are at the top. The tensile strength is calculated on the basis of the original cross-sectional area, not the actual area at point of fracture. The same fracture envelope is obtained in constant-load-creep rupture tests as in conventional stress-strain tests.

Figure 12 illustrates the effect of degree of cross-linking on failure envelopes. As expected from the previous discussion, cross-linking shifts the envelope up and to the left. Master curves for all degrees of cross-linking in the rubbery state can be obtained by dividing the tensile strength by the effective cross-link density to take care of the necessary vertical shift due to modulus changes. The curves for different degrees of cross-linking can then be superimposed to give a single curve [37]. Another method of obtaining master curves for all degrees of cross-linking is to plot $\log \lambda_B \sigma_B (T_0/T)$ against $\log E_{eB} (T_0/T)$ where E_e is the long-time equilibrium modulus of the rubber [45].

Unambiguous data on the effect of cross-linking on the stress-strain properties of rigid polymers are very scarce. However, in most cases, changing the degree of cross-linking has little effect. For long-chain rigid polymers such as polystyrene, a little cross-linking may increase the tensile strength, but high degrees of cross-linking drastically decrease tensile strength and make the polymer very brittle. For example, with styrene cross-linked by divinyl benzene, the tensile strength increases from 6700 lb/in² with no cross-linking to 7400 psi at 4% divinyl benzene; the tensile strength then drastically decreases to 1000 lb/in² at 25% divinyl benzene [46]. Theoretically, one would expect tensile strength to increase with cross-linking because weak Van der Waal's bonds are being replaced by strong covalent bonds. The decrease in tensile strength may be due to submicroscopic cracks developing from internal stresses, which result from shrinkage or thermal changes after the mobility of molecular segments has been decreased by cross-linking.

For thermoset polymers such as phenol-formaldehyde polymers, the tensile strength rapidly increases with degree of cross-linking (or cure). Such low-molecular-weight materials are extremely brittle

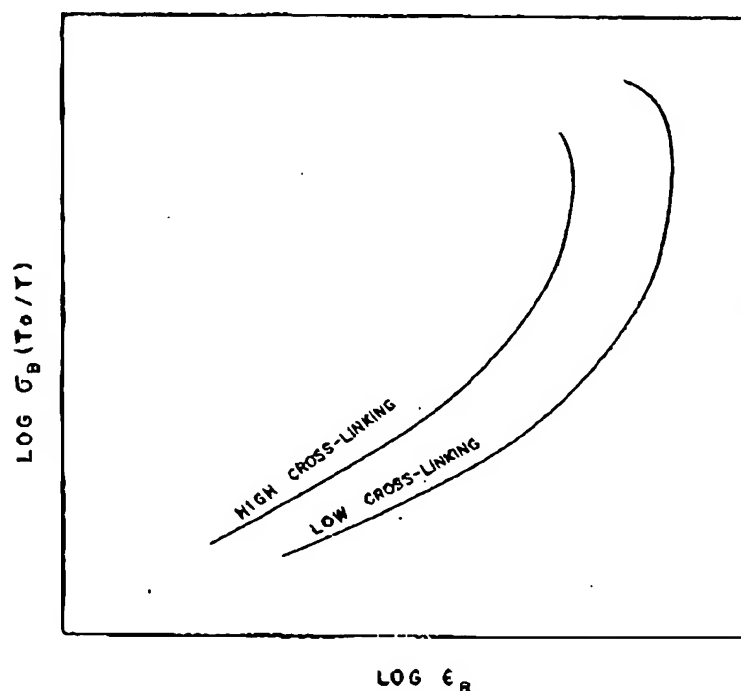


Fig. 12. Effect of cross-linking on the failure envelope of a rubber.

until the molecular weight has been built up by the curing reaction. However, above a certain stage of cure, the stress-strain properties become insensitive to the amount of cross-linking. At very high degrees of cure, the tensile strength may drop off somewhat. In all systems, but especially so with conventional thermoset polymers, the chemical structure of the polymer changes simultaneously with the degree of cross-linking. It is often impossible to decide whether it is the chemical changes or the cross-linking that is the cause of the observed effects. Radiation can sometimes be used to cross-link polymers, but often radiation simultaneously causes other effects, such as degradation, which confuse the interpretation of data [47]. Figure 13 shows how various properties of a melamine resin (a typical thermosetting polymer) change with the degree of cure [48]. Al-

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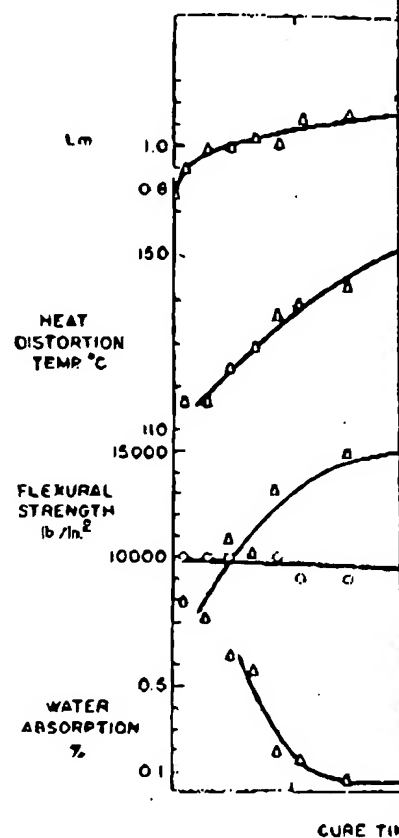
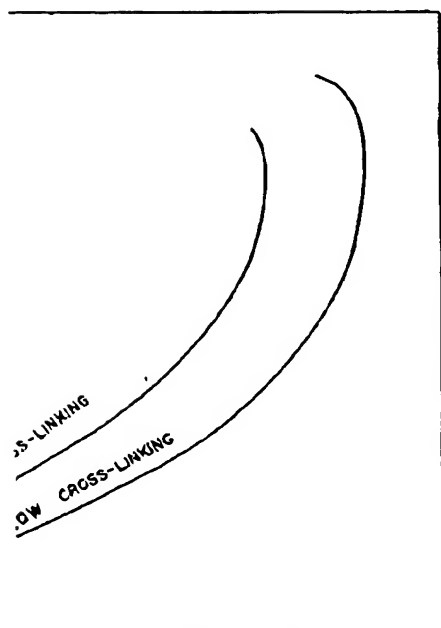


Fig. 13. Properties of an unfilled melamine resin as a function of cure time and extent of cross-linking reaction during the curing process, so on time. [Reprinted from *Ind. Eng. Chem.*, 40, 1948, copyright owner, The American Chemical Society.]

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on the failure envelope of a rubber.

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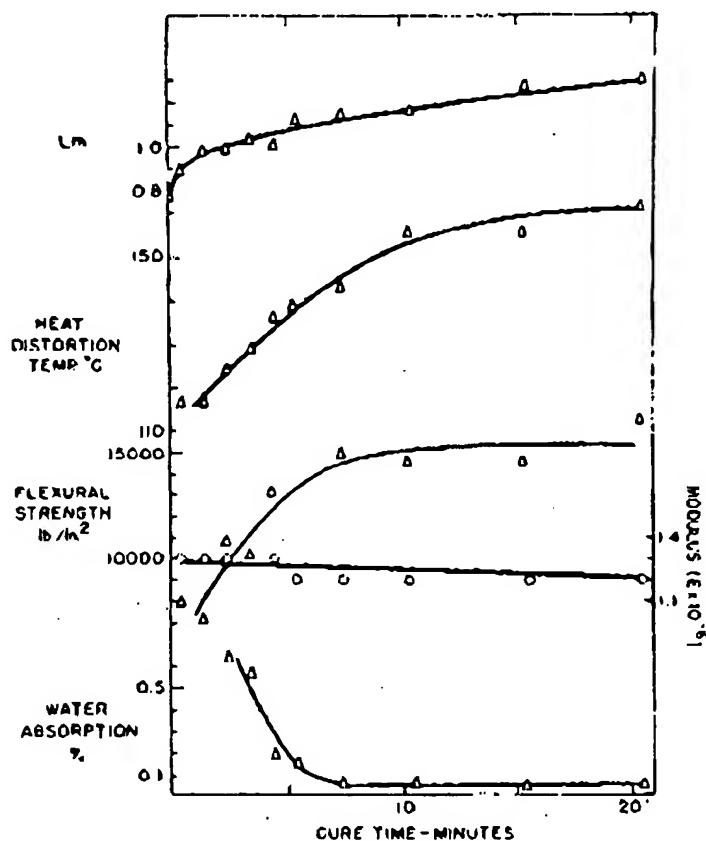


Fig. 12. Properties of an unfilled melamine resin as a function of curing time and extent of cross-linking reaction. L_m is a function of the degree of reaction during the curing process, so cross-linking increases with curing time. [Reprinted from *Ind. Eng. Chem.*, 48, 62 (1956) with permission of the copyright owner, The American Chemical Society.]

though the strength and heat-distortion temperature greatly increase with cross-linking, the modulus remains nearly constant.

Strength properties can be discussed in terms of a modified Griffith crack theory [16,49,50]. For most test specimens the following equation is applicable:

$$\sigma_B = \left(\frac{2E\gamma}{\pi C} \right)^{1/2}$$

In this equation C is the length of the flaw or crack which eventually leads to the fracture of the rigid material, and γ is the surface-energy or plastic-work function term. The surface-energy term γ is the energy required to produce a square centimeter of new surface during the fracture process. It generally consists of several factors: (1) the surface energy of the material, which is low for polymers; (2) the plastic work and molecular orientation that take place at the tip of the growing crack. This last term can be very large compared to the surface energy [50,51].

Very little information is available on how cross-linking affects flaw size C and surface work γ . At least in some cases, cross-linking decreases the surface energy for fracture and at the same time decreases the flaw size [52]. These two factors tend to counteract one another, so it is possible for the tensile strength to increase with cross-linking, if the flaw size decreases at a faster rate than the surface-energy term.

The strength and toughness of a material are increased by an increase in the surface area generated during fracture. Thus, rough fracture surfaces and many cracks rather than a single fracture crack may sometimes be desirable. This may be the reason why the experimental surface-work term increases in going from a pure cross-linked resin to a laminated fabric structure containing the resin [53].

VII. EFFECT OF CROSS-LINKING ON OTHER PROPERTIES

Cross-linking has a pronounced effect on the specific volume of a polymer and on the thermal coefficient of expansion [9,10,54,55]. For both rubbers and rigid polymers, the specific volume decreases nearly linearly with increasing density of crosslinks:

$$\bar{v} = \bar{v}_0 - k\rho \quad (18)$$

where \bar{v} is the specific volume of the cross-linked polymer, \bar{v}_0 is the specific volume of the un-cross-linked polymer, k is a constant, and ρ is the number of moles of cross-linking agent per gram of cross-

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linked polymer. A similar equation for the coefficient of thermal expansion:

$$\alpha = \alpha_0 - k'\rho$$

The coefficients of thermal expansion for cross-linked materials are α and α_0 , the latter being a physical constant. Different equations for the thermal expansion above and below T_g are different above and below T_g . Cross-linking simultaneously increases T_g and the thermal expansion region making it less and less distinct.

As might be expected, cross-linking increases the degree of crystallinity and the melting point. The effect is greater than expected if the cross-link is considered just as a co-monomer. The mobility introduced by the cross-link and crystallinity.

Cross-linking increases thermal expansion. The effect is not great even at high densities. However, this is to be expected, since the cross-linking is along covalently bonded chains rather than weak van der Waals chains, where the forces are only weak. Cross-linking has the effect of replacing weak forces by covalent ones.

Cross-linking can cut down the absorption of liquids and vapors which have not been cross-linked. This is illustrated in the case of water in Fig. 13 [48]. The absorption of water decreases as the extent of cure increases. The volume of water absorbed is the same amount as the volume of liquid taken up, the polymer pieces unless the degree of cross-linking is high enough to suppress the swelling [23,60,61]. This is one of the causes of deterioration of many polymers.

Most thermoplastic polymers can be welded together by using heat or solvents. The welding is made good contact between the two pieces. Large amounts of cross-linking greatly reduce the welding of pieces of the same material together. This has been extensively studied by Voyutskii [56].

Most of the discussion so far has been for isotropic cross-linking. However,

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distortion temperature greatly increase and remains nearly constant. It is discussed in terms of a modified [50]. For most test specimens the follow-

th of the flaw or crack which eventually rigid material, and γ is the surface-energy term. The surface-energy term γ reduce a square centimeter of new surface. It generally consists of several γ of the material, which is low for k and molecular orientation that take γ crack. This last term can be very γ energy [50,51].

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-LINKING ON OTHER PROPERTIES

ounced effect on the specific volume of a coefficient of expansion [9,10,54,55]. For iers, the specific volume decreases ng density of crosslinks:

(18)

ne of the cross-linked polymer, \bar{v}_0 is the oss-linked polymer, k is a constant, and cross-linking agent per gram of cross-

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linked polymer. A similar equation holds approximately for the coefficient of thermal expansion:

$$\alpha = \alpha_0 - k'p \quad (19)$$

The coefficients of thermal expansion for the cross-linked and uncross-linked materials are α and α_0 , respectively, and k' is an empirical constant. Different equations hold for the specific volume and the thermal expansion above and below T_g , i.e., the values of k and k' are different above and below T_g . As mentioned earlier, cross-linking simultaneously increases T_g and broadens the transition region making it less and less distinct as cross-linking progresses.

As might be expected, cross-linking greatly reduces the degree of crystallinity and the melting point of crystallizable polymers [56]. The effect is greater than expected if the cross-linking agent is considered just as a co-monomer. The added restrictions on chain mobility introduced by the cross-links also reduces melting points and crystallinity.

Cross-linking increases thermal conductivity slightly [57,58]. The effect is not great even at high degrees of cross-linking. However, this is to be expected, since the flow of heat tends to be greater along covalently bonded chains than in directions perpendicular to chains, where the forces are only weak Van der Waals' forces. Cross-linking has the effect of replacing some of the Van der Waals' forces by covalent ones.

Cross-linking can cut down the absorption and swelling of polymers in liquids and vapors which have some affinity for the polymer. This is illustrated in the case of water absorption in a melamine resin in Fig. 13 [46]. The absorption of water decreases as the extent of cure increases. The volume of a polymer increases roughly the same amount as the volume of liquid absorbed [59]. Thus, if too much liquid is taken up, the polymer may be fractured into many pieces unless the degree of cross-linking is high enough to greatly suppress the swelling [23,60,61]. This fracture process may be one of the causes of deterioration of many composite materials by water.

Most thermoplastic polymers can be welded or made to adhere to themselves by using heat or solvents along with some pressure to make good contact between the two pieces of polymer. Even small amounts of cross-linking greatly reduce the ease of welding two pieces of the same material together. This field of autohesion has been extensively studied by Voyutskii [62].

Most of the discussion so far has been related to what might be called isotropic cross-linking. However, anisotropic network struc-

tures can also be formed. One way of forming anisotropic networks is to partially cross-link a rubber; then the rubber is stretched and the cross-linking is continued to completion. Such a process essentially superimposes two types of networks in one polymer. Such materials show properties due to cross-linking similar to what has already been discussed, except that anisotropic network polymer may show somewhat different properties in different directions. The modulus of anisotropic rubbers is increased in the direction parallel to the direction of stretch, while the elongation to break is decreased in the direction of the original stretch [63-65]. Swelling tends to be greater in the direction perpendicular to the original direction of stretch. Several papers on the theory and experimental results of anisotropic networks have been published [66-68].

VIII. SUMMARY

Cross-linked network structures can be very complex and varied, and our tools for studying and characterizing such structures are not adequate. The techniques for studying high degrees of cross-linking and cross-linking in the solid state are especially poor. For this reason, clear-cut data showing how cross-linking affects various physical properties is limited, and more good scientific work is needed both for developing techniques and for determining the relation of physical properties to cross-linking.

IX. GLOSSARY OF

| | |
|--------------------|--|
| b | Branching coefficient |
| b_c | Critical value of branching coefficient occurs |
| C | Length of a Griffith crack or |
| C_x | Number of moles of tetrafunctional unit volume of polymer |
| d | Density of polymer |
| d_M | Density of un-cross-linked polymer |
| d_x | Density of cross-linked polymer |
| E | Young's modulus |
| E_e | Long-time-equilibrium Young's modulus |
| f | Functionality of the cross-linking agent |
| F_M | Segmental mobility of un-cross-linked polymer |
| F_x | Segmental mobility of cross-linked polymer |
| G | Shear modulus |
| k | A constant |
| k' | A constant |
| M | Molecular weight of un-cross-linked polymer (number average) |
| M_n | Number-average molecular weight of polymer |
| M_c | Number-average molecular weight of cross-linked points |
| $(M_o)_M$ | Molecular weight of an un-cross-linked polymer |
| $(M_o)_x$ | Molecular weight of a cross-linked polymer |
| n | Number of moles of network polymer |
| n_c | Average number of atoms in cross-links |
| N | Avogadro's number |
| p | Extent of gelation reaction |
| P | Pressure |
| q | Swelling ratio |
| $\overline{r^2}$ | Mean-square distance between cross-links |
| $\overline{r^2}_0$ | Mean-square end-to-end distance in space |
| R | Gas constant |
| T | Temperature ($^{\circ}\text{K}$) |
| T_0 | Reference temperature |
| T_g | Glass-transition temperature |

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One way of forming anisotropic networks rubber; then the rubber is stretched and led to completion. Such a process essentially of networks in one polymer. Such due to cross-linking similar to what has except that anisotropic network polymer may properties in different directions. The bers is increased in the direction parallel while the elongation to break is decreased nal stretch [63-65]. Swelling tends to be pendicular to the original direction of the theory and experimental results of been published [66-68].

III. SUMMARY

Structures can be very complex and varied, and characterizing such structures are as for studying high degrees of cross-linking in the solid state are especially poor. For showing how cross-linking affects various ted, and more good scientific work is techniques and for determining the relation to cross-linking.

IX. GLOSSARY OF SYMBOLS

| | |
|--------------------|---|
| b | Branching coefficient |
| b_c | Critical value of branching coefficient at which first gelation occurs |
| C | Length of a Griffith crack or flaw |
| C_x | Number of moles of tetrafunctional cross-linking agent per unit volume of polymer |
| d | Density of polymer |
| d_M | Density of un-cross-linked polymer |
| d_x | Density of cross-linked polymer |
| E | Young's modulus |
| E_e | Long-time-equilibrium Young's modulus of a rubber |
| f | Functionality of the cross-linking agent |
| F_M | Segmental mobility of un-cross-linked polymer |
| F_x | Segmental mobility of cross-linked polymer |
| G | Shear modulus |
| k | A constant |
| k' | A constant |
| M | Molecular weight of un-cross-linked polymer (generally number average) |
| M_n | Number-average molecular weight of un-cross-linked polymer |
| M_c | Number-average molecular weight of polymer between cross-linked points |
| $(Mo)_M$ | Molecular weight of an un-cross-linked monomer unit |
| $(Mo)_x$ | Molecular weight of a cross-linked monomer unit |
| n | Number of moles of network chains per unit volume of polymer |
| n_c | Average number of atoms in polymer backbone between cross-links |
| N | Avogadro's number |
| p | Extent of gelation reaction |
| P | Pressure |
| q | Swelling ratio |
| $\overline{r^2}$ | Mean-square distance between network junctures |
| $\overline{r_0^2}$ | Mean-square end-to-end distance of network chains in free space |
| R | Gas constant |
| T | Temperature ($^{\circ}\text{K}$) |
| T_0 | Reference temperature |
| T_g | Glass-transition temperature ($^{\circ}\text{K}$ in theoretical equations) |

| | |
|--------------|---|
| T_{ga} | Glass-transition temperature of the un-cross-linked polymer having the same chemical composition as the cross-linked polymer |
| \bar{V} | Specific volume of polymer |
| v_2 | Volume fraction of polymer in swollen polymer |
| V_1 | Molar volume of solvent |
| X | Mole fraction of polymer that is not cross-linking agent |
| X_c | Mole fraction of monomeric units which are cross-linked |
| α | Coefficient of thermal expansion of cross-linked polymer |
| α_0 | Coefficient of thermal expansion of un-cross-linked polymer |
| γ | Surface energy or plastic work function |
| δ_M | Solubility parameter of un-cross-linked polymer |
| δ_X | Solubility parameter of cross-linked polymer |
| ϵ_M | Lattice energy of un-cross-linked polymer |
| ϵ_X | Lattice energy of cross-linked polymer |
| θ | Ratio of hydroxyl groups belonging to the trifunctional alcohol to the total number of hydroxyl groups in a mixture of di- and trifunctional alcohols |
| λ_B | Extension ratio to break |
| ν | Number of cross-linked chains per unit volume of polymer |
| ν_e | Effective number of cross-linked chains per unit volume |
| ρ | Number of moles of cross-links per gram of final polymer |
| σ_B | Tensile strength of polymer |
| χ | Interaction parameter between polymer and solvent |

ACKNOWLEDGMENT

This work was sponsored by the Advanced Research Projects Agency Department of Defense, through contract with the Office of Naval Research N00014-67-C-0218 (formerly N00014-66-C-0045), ARPA Order No. 873, ONR contract authority NR. 356-484/4-13-86, "Development of High-Performance Composites."

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temperature of the un-cross-linked polymer
chemical composition as the cross-

polymer.

polymer in swollen polymer
liquid

polymer that is not cross-linking agent
monomeric units which are cross-linked
thermal expansion of cross-linked polymer
thermal expansion of un-cross-linked polymer
elastic work function
ratio of un-cross-linked polymer
ratio of cross-linked polymer
ratio of cross-linked polymer
cross-linked polymer
groups belonging to the trifunctional
number of hydroxyl groups in a mix-
functional alcohols
break

linked chains per unit volume of polymer
of cross-linked chains per unit volume
of cross-links per gram of final polymer
polymer
ratio between polymer and solvent

ACKNOWLEDGMENT

supported by the Advanced Research Projects
Agency, through contract with the Office of
Naval Research (formerly N00014-66-C-0045),
contract authority NR. 356-484/4-13-66,
Performance Composites."

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